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Dynamic and static radiation scattering in a microemulsion as a function of dispersed phase concentration

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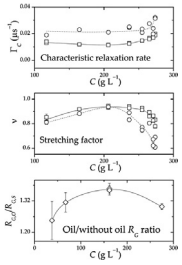
HIGHLIGHTS

- DLS and SAXS can be used to characterize sphere/worm-like transitions in microemulsions.
- Increase in characteristic relaxation rate from DLS indicates this transition.
- Broadening of relaxation rate distribution from DLS is caused by an increase in micellar dimensions.
- SAXS indicates that oil phase inhibits the formation of worm-like structures.

GRAPHICAL ABSTRACT



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ABSTRACT

Dynamic light scattering and SAXS were used to characterize the change in dimensions of the dispersed phase in microemulsions based on $C_{12}E_9$ non-ionic surfactant, butanol, xylene, and water, as a function of dispersed phase concentration. A KWW-based equation was fitted to data from intensity correlation functions of the microemulsions and a transition from spherical to worm-like geometry was related to a decrease in the dimensions of the randomly oscillating regions of the resultant systems as well as to the broadening of their characteristic relaxation rate distributions. More specifically, the transition was characterized by an increase in the characteristic relaxation rate as well as by a decrease in the stretching coefficient (related to an increased heterogeneity of more complex colloidal structures). Static SAXS was used to characterize the transition as occurring at the maximum ratio between the radii of gyration of the system with and without xylene, which was shown to me correlated to previously obtained data associating this transition to a maximum in the ratio of viscosities for the same systems.

1. Introduction

Microemulsions are clear and thermodynamic stable mixtures, normally consisting of a surfactant, a co-surfactant, oil, and water [1], which have becoming increasingly more important for vast range of applications [2]. In materials science they have been used to obtain both organic and inorganic nanoparticles [3–6] and some systems have successfully been used in enhanced oil recovery [7]. In environmental applications (more specifically in soil remediation), they can be used to wash out polycyclic aromatic hydrocarbons [8] and have intensely been used/suggested for pharmaceutical formulations destined to controlled release of bioactive agents [9]. It has also found its place in analytical chemistry: microemulsion electrokinetic chromatography (MEEKC) has been proven to be both

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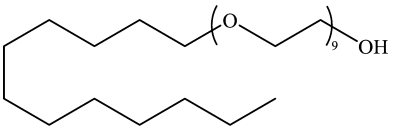

Fig. 1. Chemical structure of ALKONAT L90.

an excellent technique for separation and a potent analytical tool [10].

Microemulsions specifically based on non-ionic surfactants have found extensive usage in oil exploration [11]. Among these non-ionic surfactants, polyethoxylated alkyl ones (C_nE_m, where n is the number of carbons of the hydrophobic and saturated linear chain, and m is the number of ethoxy groups in the polar head) [12] are one of the most useful surface-active substances, attracting the interest of the scientific community, due to their remarkable and unique properties [13–15]. In the oil industry, they have been used in metalworking fluids [16], drilling fluid formulations [17] as well as systems with biocide activity [18].

Micellar systems based on C_nE_m may spontaneously form micelles with wormlike geometries [19,20]. These association colloids have unusual characteristics due to its supramolecular structures resembling macromolecular coils (or rods, for lower aggregation numbers) [19,21]. Hence, some similarities between polymer and worm-like micelle solutions have been observed: *e.g.*, a dependence of intrinsic viscosity/dynamic light scattering parameters on worm-like micelle dimensions [22–24], and a rheological behavior that, depending on experimental conditions (*e.g.* shear rate and temperature), may be shear-thickening or -thinning [25,26]. Several methods have been used to characterize the occurrence of wormlike structures (some of them in microemulsion-based systems [27]): *e.g.*, the transition between nanodrop to wormlike geometries has been characterized using rheological measurements [28–31] and static scattering techniques [32–34]. Dynamic light scattering (DLS) was shown to be a technique that, for these systems, gives some results that may have a dubious interpretation, regarding colloidal dimensions: as diameter distribution is determined from the distribution of particle relaxation rates and the viscosity of the continuous phase, the definition of what exactly is the continuous phase (*i.e.*, pure water or a solution of non-associated surfactant molecules?), results in a problem of difficult interpretation [35].

As a result of all these questions, our group approached DLS not as a form of determining micellar dimensions of these systems: we tried to characterize possible transitions as a consequence of relaxations bound to random movements of these structures (or part of them) in solution [36], in the same way it has been used for polymer solutions [37,38] and even C_nE_m/polymer ones [39]. The aim of the present work is to associate DLS measurements to static small angle X-ray scattering (SAXS) measurements in order to obtain an analysis that will take into account the dynamic of these structures in solution, as well as their overall dimensions. Finally, a more accurate comprehension of why the maximum in the ratio between the viscosity of the microemulsion with oil phase and the viscosity of the system without oil phase [36] can be used as an indication of sphere to worm-like geometry transition.

2. Experimental

2.1. Materials

Nonaethyleneglycol-monododecylether (ALKONAT L90, Oxiteno, Brazil, Fig. 1), *n*-butanol (P.A., Synth Brazil), xylene (P.A., Synth Brazil) were used as received. Water used in the experiments was bi-distilled.

Table 1
Composition of the microemulsion used in this work.

Parameter	Value
Surfactant to co-surfactant mass ratio	0.5
Water mass fraction	0.55
Oil mass fraction	0.05
Surfactant + co-surfactant mass fraction	0.40

2.2. Microemulsion preparation

The microemulsion used in this work consisted of ALKONAT L90 (surfactant), *n*-butanol (co-surfactant), xylene (oil phase), and bi-distilled water with the composition displayed in Table 1. In a previous work we found that at this composition the ternary diagram indicated that the system could continuously be diluted in water without departing from the microemulsion region [36].

The density of this composition, ρ, was determined by picnometry, in order that one could be able to calculate surface active agents (surfactant + co-surfactant) mass/volume concentration, C, according to

$$C = \rho w \quad (1)$$

where w is the mass fraction of surface active agents (surfactant + co-surfactant). The influence of the following parameters was analyzed:

(1) Surface active agents concentration, adjusted by dilution of the microemulsion with bi-distilled water.
(2) The presence or absence of the oil phase (xylene) in the system.

2.3. Dynamic light scattering

Dynamic light scattering experiments were carried out with the dispersions using a 90 Plus Particle Analyzer (Brookhaven Instruments Corporation, USA). All the samples were filtered using Durapore membrane filters with pore size of 0.22 μm. Data related to the intensity correlation function (ICF), $g^{(2)}(t_D)$, where t_D is the delay time, were collected at a temperature of $(25.0 \pm 0.1)\,^{\circ}C$.

2.4. Small angle X-ray scattering

SAXS experiments were carried out using a SAXSess camera (Anton Paar, Austria), connected to a laboratorial generator of X-rays ISO-DEBYEFLEX 3003 (GE Inspection Technologies GmbH, Germany), with radiation of Cu Kα of wavelength of 0.1542 nm. This generator was operated under a voltage of 40 kV and current of 50 mA. The samples were sealed under vacuum in a quartz capillary with an external diameter of 1 mm and thickness of 10 μm. The measures of scattering intensity were performed on an image plate with a detection system of Cyclone Plus (Perkin Elmer, USA) and converted to dimensionless intensity by the SAXSquant 3.50 software (Anton Paar GmbH, Austria). The experiments were performed applying an exposition to the light beam for a period of 30 minutes for all samples; we also performed blanks of each solvent to determine the experimental scattering curves. The distance between the sample and detector was fixed in 700 mm, which allowed us to carry out the experiments with the scattering angle defined as:

$$q = \frac{4\pi}{\lambda} \sin\theta \quad (2)$$

in which λ is the wavelength of the radiation and 2θ is the scattering angle. The thermostated sample holder (TCS 120, Anton Paar GmbH, Austria) was kept at 25 °C. The average gyration radius, R_G,